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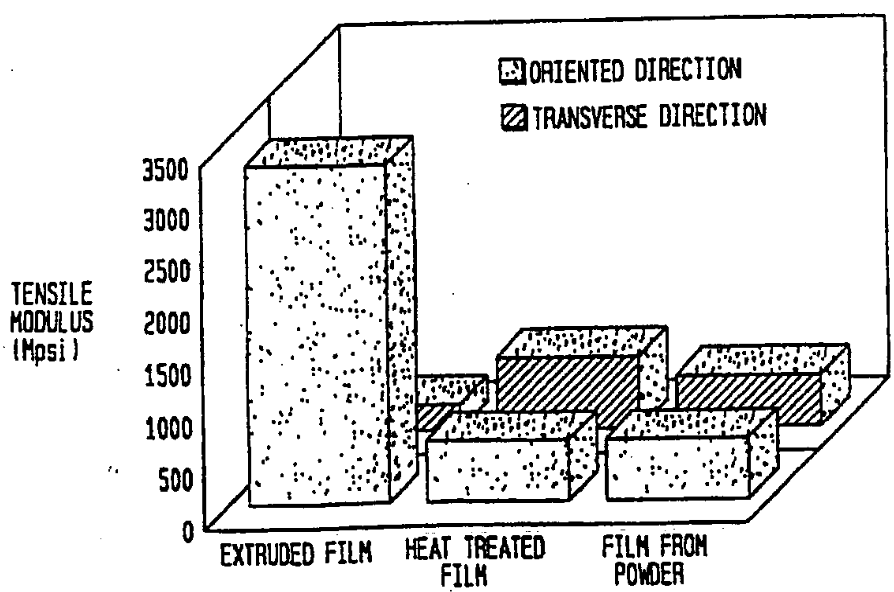

(57) Abstract

Liquid crystal polymer films and film laminates are prepared by subjecting finely divided polymer particles to sufficient heat and pressure to form a nematic melt phase of the polymer and cooling the structure to form a film. Films prepared by this process exhibit a better balance of tensile properties, improved dimensional stability and reduced coefficient of thermal expansion than conventional extruded film, rendering them more suitable as dielectric film layers in circuit board construction.

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LIQUID CRYSTAL POLYMER FILMS

Field of the Invention

The invention relates to the field of polymer films, particularly liquid crystalline polymer (LCP) films.

Description of Related Art

A variety of thermotropic liquid crystal polymers and films made therefrom are known in the art. For example, U.S. Pat. No. 4,161,470 discloses a polyester of 6-hydroxy-2-naphthoic acid and p-hydroxy benzoic acid capable of undergoing melt processing. U.S. Pat. No. 4,184,966 discloses melt processible, thermotropic, wholly aromatic polyesters, and U.S. Pat. No. 4,279,803 discloses a polyester of phenyl-4-hydroxybenzoic and 4-hydroxybenzoic acid and/or 6-hydroxy-2-naphthoic acid.

Liquid crystalline polymer film or sheet has a number of well-known applications, including some that involve a lamination process. Examples include tape winding composite structures, cross lamination to provide balanced mechanical properties or thick structures, metal lamination for circuits, or lamination of circuit/dielectric layers for multilayer circuit boards.

Due to the particular molecular structure of thermotropic liquid crystal polymers, LCP film can be molecularly oriented in the melt phase, uniaxially, biaxially, or otherwise. After the extruded LCP cools and solidifies, the molecular orientation is maintained, resulting in a film which may have anisotropic properties, such as enhanced mechanical properties in the direction(s) of orientation, e.g., high strength and stiffness.

The conventional technique for producing oriented LCP film involves introducing polymer pellets into a melt extruder and melt extruding a sheet of film which is drawn in the machine direction to produce monoaxially oriented film. Biaxially oriented film is prepared by casting a molten sheet of the polymer onto a casting drum and then stretching (orientating) the cast sheet in a tenter frame apparatus in the longitudinal (machine) direction and in the lateral (transverse) direction to produce biaxially oriented isotropic film. A tubular film inflation process can also be used to produce such film.

Film produced by such methods is perfectly suitable for most applications such as packaging or tape applications. However, in other applications such as where the film is used as a dielectric layer or wiring module board in the construction of multi-layer circuit boards, it is necessary that the film be as uniformly dimensionally stable as possible.

Oriented film can exhibit shape changes, shrinking, curling, and other distortions when heated in accordance with circuit board fabrication techniques. This distortion is caused primarily as the result of an imbalance of tensile modulus, tensile strength, tensile elongation, shrinkage and expansion properties as a function of the direction of film orientation. The resulting film distortion can adversely affect the integrity of the printed circuit board and can lead to circuit failure or lamination failure between adjacent laminated surfaces. In addition, LCP film produced by conventional extrusion methods can have a number of defects such as holes, gels, black specks, gauge

variability and the like which can detract from the dielectric properties of the film in circuit board applications.

One technique for improving the mechanical property balance in film material made from polyphenylene sulfide polymers, as disclosed in U.S. Patent 4,389,453, is to incorporate chopped glass fibers into the polymer prior to extrusion or press molding the composition into a composite sheet material suited for circuit board construction. Such sheets may also be formed by heat compressing a woven glass mat with a film of the polymer or heat compressing a glass mat containing the polymer in powdery, particulate form.

Another technique addressing heat distortion problems is to prepare uniaxially oriented LCP film and subsequently thermally laminate a plurality of such films together with their axes of orientation aligned in different directions in an attempt to balance out the mechanical properties of the laminated structure, as disclosed in U.S. Patent 4,384,016.

However, these and other methods involve additional processing steps which add to the cost of such films and leave open the possibility of processing errors.

SUMMARY OF THE INVENTION

The present invention provides process for producing a continuous liquid crystal polymer film material having balanced dimensional stability comprising: (a) uniformly spreading a layer of powder particles of said polymer on a flat surface, said particles having an average particle

size in the range of about 0.5 to about 250 microns; (b) superimposing a second flat surface over said uniformly spread particles to form a sandwich structure; (c) subjecting said sandwich structure to uniform heat and pressure sufficient to form a nematic melt phase of said polymer; and (d) cooling said structure to form a liquid crystalline film.

The films produced according to the process of the invention demonstrate an improved balance of tensile strength, tensile modulus and tensile elongation properties as well as a balanced coefficient of thermal expansion compared with conventional films made by extrusion and mono- or biaxial orientation processes. These balanced properties render the film less susceptible to heat distortion when used as insulating dielectric layers in the construction of microelectronic circuit boards.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph depicting tensile modulus balance for films prepared from powder polymer vs other films as shown in Table 1.

Fig. 2 is a graph depicting tensile strength balance for films prepared from powder polymer vs other films as also shown in Table 1.

Fig. 3 is a graph depicting coefficient of thermal expansion (CTE) values for films prepared from powder polymer vs other films as shown in Table 2.

Fig. 4 is a graph depicting CTE values for 2 and 4 mil

double sided, copper foil laminated film, as shown in Table 2.

Fig. 5 is a graph depicting dimensional stability values for 2 mil double sided, copper foil laminated film after baking the film, as shown in Table 3.

DETAILED DESCRIPTION OF THE INVENTION

The liquid crystalline polymers (LCP) used in the present invention are preferably thermoplastic polyester polymers containing rigid mesogenic linkages. These polymers generally have crystalline melting points in the range of from about 250°C to 375°C, more preferably from about 270°C to 355°C. Suitable polymers which may be used as polymer components in the production of films include polyesters comprising monomer units derived from 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid; a polyester comprising monomer units derived from 6-hydroxy-2-naphthoic acid, terephthalic acid, and acetaminophen; and a polyester comprising monomer units derived from 4-hydroxybenzoic acid, terephthalic acid and 4,4'-biphenol.

Particularly preferred polyesters and polyester-amides are those available from Hoechst Celanese Corporation under the trademark VECTRA®. These include VECTRA® A polyester, VECTRA® C polyester, VECTRA® E polyester, and VECTRA® B polyester-amide.

It is also within the scope of the present invention to use liquid crystal polymers other than the VECTRA® polyesters described above. Generally, any such polymers that can be consolidated under heat and pressure to form

a nematic LCP melt may be used in practicing this invention. Examples of such liquid crystal polymers include, but are not limited to XYDAR® LCP (a polyester made by Amoco Co.) comprising units derived from HBA, TA, 4,4'-biphenyl, DuPont's Zenite LCP, as well as other mesogenic group-containing LCP's.

The polymers are processed in the present process in the form of particles having an average particle size of about 0.5 to 250 microns, more preferably from about 0.5 to 5 microns.

A liquid crystal polymer can be polymerized in a dispersion process which provides the product in powder form. In this process the polymer is prepared in the form of a fine dispersion in a liquid medium. The polymer dispersion is created by heating the monomers with a catalyst in the liquid under high shear mixing, and the resulting polymer particles are stabilized by an agent that coats the surface of the particle to prevent particles from coalescing. The monomers may be soluble in the liquid medium, but complete solubility is not required. A variety of liquids or dispersion stabilizing agents that are sufficiently stable under the polymerization conditions may be used to prepare a liquid crystal polymer powder. The polymer powder must be separated from the liquid and washed to remove residual liquid. The dry powder is free flowing and the particles are generally uniform spherical particles. The particle size distribution depends on the dispersion conditions. Mechanical grinding of a liquid crystal polymer prepared in a conventional bulk melt polymerization does not produce the same free flowing powder form.

Films are produced by uniformly spreading or spraying the polymer powder on a flat surface which may be release film such as a silicone or polyimide film or a conductive metallic non-release film such as copper, aluminum or silver foil, preferably copper foil. The particles should be spread as evenly and uniformly as possible using a spreader such as the edge of a coarse wire mesh screen. The quantity and thickness of powder applied to the support should be sufficient such that the films produced after thermal consolidation have a thickness of from about 0.25 to 10 mils, more preferably from about 1 to 5 mils.

In the next step, a second flat surface is superimposed over the uniformly spread particles supported on the first flat surface to form a sandwich structure. This second surface may also be a release film or metal foil. Both flat surfaces may be release films or metal foils or one may be a release film and the other a metal foil.

In the next step, the sandwich structure is subjected to uniform heat and pressure sufficient to form a nematic melt of the polymer sandwiched between the outer sheets or foils, followed by cooling the film. This may be accomplished by placing the structure in a conventional laminating press having heated platens or, more preferably, by inserting the structure between a pair of heated moving double belts which compress, consolidate and heat the powder sufficiently to form a nematic melt. In general, the sandwich structure is heated to a temperature in the range of from about 25°C below the melting point of the polymer being processed to about 50°C above such melting point. The most preferred heating temperature is from about the melting point up to

about 15 to 35°C above the melting point of the polymer being processed. Pressures in the processing zone may range from about 50 to 600 psi, more preferably from about 400-500 psi. Residence time in the processing zone may range from about 0.25 to 5 minutes, preferably from about 1 to 1.5 minutes.

The double belt press used to produce the film and laminate in the preferred embodiment has two steel belts each traveling around a pair of rotating drums. The belt surfaces travel parallel to one another and in close proximity to form the processing section. A constant pressure is maintained on the sample by pressurized oil behind each belt. The belts are heated by the inlet drums, and further heated by four heating zones which transfer heat to the belt and ultimately to the product. Next, the material passes through two cooling zones before exiting the processing station. The length of the processing section is 2.5 m and the width of the belts is 1.4 m.

The temperature of the inlet drum, heating zones, and cooling zones should be such that the product is raised to the proper temperature long enough for complete consolidation. Before exiting, it should be cooled to a temperature below the softening point, at which flexing will not result in permanent deformation. The inlet drum is set to a temperature between ambient and consolidation temperature, but most preferably at 220°C or below in order to avoid oxidation and discoloring of copper foil while it is exposed to the atmosphere in case a laminate is being produced. The first heating zone is controlled at a temperature between that of the inlet drum and the consolidation temperature, preferably about 10°C below

the melt temperature to insure that the material is well into the pressurized area before melting. The second, third, and fourth heating zones are set at the consolidation temperature. As stated above, this temperature is preferably between 25°C below the melt point of the material being processed to 50°C above the melt point, but most preferably is about 25°C above the melt temperature. The first cooling zone should begin reducing the product temperature to a point at least 10°C below its melting point. The second cooling zone determines the exit temperature of the product, which should be below 220°C if copper laminate is being produced. Further, this temperature should be low enough that any flexing does not result in permanent deformation of the final product. The pressure in the processing zone can be between about 50 psi to 600 psi, but preferably should be about 450 psi. The belt speed can be set to give a residence time in the processing zone of 0.25 to 5 minutes but preferably 1.2 minutes for 2 mm thick belts. The belt speed is limited by the capacity of the cooling zones to bring the belts down to the desired exit temperature.

The cooled LCP film is then recovered by peeling away the non-adherent release layer(s). Where one or both layers are metallic layers, these will remain adhered to the film and serve as etching layers for the formation of electrical circuit patterns on one or both surfaces of the film by techniques well known in the art. These metallic layers may also be subsequently applied to the film surface by known methods such as foil lamination or vapor deposition techniques. In general, the thickness of these metallic layers may range from about 0.25 to 6 mils, more preferably from 1.5 to 5.4 mils.

Multilayer microelectronic circuit boards may be fabricated by stacking and laminating a plurality of circuit layers containing wiring and/or drilled conductive vias present on the LCP sheets of the invention. The circuit layer sheets are stacked in appropriate electrical registration and thermally compressed, during which process the thermoplastic properties of the sheets, or any adhesive which may be applied between adjacent sheets, cause the sheets to bond together to provide a multilayer printed circuit board of mechanical integrity.

The production of film and laminates from LCP powder represents a streamlined manufacturing process which eliminates the need to extrude film, and results in a film having an improved balance of mechanical properties and lower coefficient of thermal expansion than extruded or axially oriented film. These enhanced properties translate into reduced tendency for the film to crack or distort when subjected to conditions encountered during the fabrication of printed circuit boards, e.g. reduced cracking around plated through holes (vias) and reduced potential for disruption of wiring circuitry.

The following examples are illustrative of the invention. The polymer used in the following experiments, from which the referenced powder and film products were made, was a polyester comprising about 73 mole % of monomer units derived from 4-hydroxybenzoic acid and about 27 mole % of monomer units derived from 6-hydroxy-2-naphthoic acid, and having a melting point of about 280-282°C.

Preparation of polymer powder is illustrated in Example 1.

EXAMPLE 1

Polymer polymerization was done in a 4 liter 2-piece cylindrically shaped flask fitted with a stirrer, nitrogen inlet, vigreux column with trap, and thermocouple. One or two stainless steel agitators (high shear radial flow impeller) were attached to the stainless steel stirring rod. A condenser was attached to the vigreux column. At the end of the condenser was an elbow which extended into a graduated cylinder, the receiving vessel.

	Materials (supplier)	Weight
Monomers	4-hydroxybenzoic acid (Ueno) 6-hydroxy-2-naphthoic acid (Ueno)	604.4 304.6
Dispersing Agent	Bentone 38 (Rheox) Propylene carbonate (Aldrich)	23.2 6.4
Liquid Medium	Mineral oil, Kaydol (Ruger)	1161
Acetylating Agent	Acetic anhydride	631.6*
Catalyst	Potassium acetate (120 ppm K+ based on polymer)	0.24●

* The amount of acetic anhydride is corrected for purity based on the lot analysis and an excess of 2.5% is added.

The monomers and catalyst were added to the flask which was placed in the sandbath. The flask was purged with nitrogen, overnight for convenience. The dispersing medium was prepared by mixing Bentone 38 and 500 g of mineral oil in an explosion proof laboratory blender (Waring) for about 5 minutes. Propylene carbonate was added and mixing was continued for about 2 more minutes. The viscous mixture was then added to the flask

containing the monomers while purging with nitrogen. The remaining mineral oil was added to the blender and mixed for about 2 more minutes before adding it to the flask. The acetic anhydride was used to rinse the blender and added to the flask. The temperature program and stirrer (150 rpm) were started.

A Micricon programmer was used to control the temperature. The reaction flask was heated from room temperature to a final temperature 300-340°C over a period of about 4 hours, under nitrogen, while stirring. The heating profile is described below. The mixture was heated at about 1°/min. for the first two hours. Acetic acid by-product begins to distill from the flask when the temperature reaches about 150°C. The heating rate was decreased to 0.66°/min. until a temperature of 190°C was reached. The stirring rate was increased from 150 to 500 rpm. Heating was continued at a rate of 2°/min. and reduced to 0.5°/min. only for the last 15°.

The remaining acetic acid distilled from the flask and a total of about 2 equivalents were collected. The reaction mixture was held at a final temperature for 20 to 60 minutes. The final temperature generally ranged from 300° to 340°C. At the end of the hold time, the heating source was lowered and stirring was continued at 500 rpm until the temperature fell below 200°C (polymer has solidified). The stirring rate was reduced to about 100 rpm and the flask cooled to room temperature.

The polymer was filtered from the liquid using a Buchner funnel with coarse filter paper. The powder was washed twice with toluene to remove the mineral oil, air dried, and then dried in an oven (100°C). The powder was sieved

with 180 μm sieve.

EXAMPLE 2

Film from powder as prepared in Example 1 was made by applying a pre weighed amount of the powder on a flat film surface, which was either a polyimide release film or a copper foil as indicated below, within an 18 inch by 18 inch area. The powder was spread evenly within this area using the edge of a coarse wire screen. A second film (either release or copper film) was then superimposed over the powder to form a sandwich structure. The sandwich was then introduced between the belts of a double metal moving belt press.

The belt speed was set at 2m/min. and the processing zone pressure was 30 bar. Temperature observations and zone lengths are shown below:

Inlet Drum	218+/-1°C	
Heat Zone 1	270°C	30 cm in length
Heat Zone 2	304+/-1°C	30 cm in length
Heat Zone 3	305+/-1°C	30 cm in length
Heat Zone 4	306+/-1°C	60 cm in length
Cooling Zone 1	249+/-13°C	30 cm in length
Cooling Zone 2	195+/-2°C	30 cm in length

Any variation in the process temperatures is the result of control limitations rather than deliberate changes in set point.

COMPARATIVE EXAMPLE 3

For comparative purposes, preformed sheets of extruded

film (monoaxially oriented) prepared using VECTRA A polymer were also passed through the belt press under the conditions set forth above. These films were fed to the belt press with their extrusion direction parallel to the travel direction of the belts through the press.

In the following Tables, various types of film are evaluated for tensile, shrinkage, tear strength and coefficient of thermal expansion (CTE). The construction of films referred to in the Tables was as follows:

2 Mil Film -	Monoaxially oriented, extruded film treated in the belt press as described above.
2X2 Mil Film -	Two layer laminate of two Mil film treated in the belt press as described above.
Powder -	Film made from polymer powder treated in the belt press as described above.
Single Sided Laminate -	Film having a single sheet of copper foil laminated to one side.
Double Sided Laminate -	Film having two sheets of copper foil laminated to both sides.
Extruded Film -	2 Mil, monoaxially oriented extruded film not subject to further heat treatment (control).

The mechanical properties of the film were evaluated in accordance with the following test procedures. Testing for tensile strength, tensile modulus, and elongation was done according to ASTM D882, the 190°C shrinkage test used method ASTM D1204, and the method used for tear strength was ASTM D1938. The coefficient of thermal expansion testing was done using a Perkin Elmer Delta Series TMA 7 Thermo-Mechanical Analyzer. Machine Direction and Transverse Direction measurements were made in the extension mode using samples approximately 2.5 mm x 12 mm in size. Thickness (Z-Direction) measurements were made in the expansion mode using 6 mm diameter circular samples stacked to a total height of about 0.5 to 1.5 mm. Dimensional Stability measurements were made according to IPC-TM-650 2.2.4, Method B (as etched) and Method C (baked).

Mechanical properties of the film samples are shown in Table 1 along with the properties of the 2 mil extruded film (control). Tear strength results indicate that each of the samples tended to tear preferentially in one direction, either the machine direction (MD) or transverse direction (TD). The extruded control is quite unbalanced with most of the orientation in the machine direction. The heat treated films and the film produced from powder both exhibit more balanced properties, although each sample tends to have somewhat more orientation in one direction or the other. The direction of greater orientation exhibits higher mechanical properties and lower CTE. Fig. 1 compares the tensile modulus of the extruded film, heat treated film, and the film from powder. The heat treated and powder films are more balanced and have almost the same modulus values. Fig. 2 is a similar graph showing tensile strength, which

is also more balanced for the heat treated and powder films. The tensile strength of the powder film as might be expected, is lower due to its lower level of orientation. CTE was measured on a number of additional film samples including films laminated with copper foil which was removed by etching prior to testing of the film. The results of these measurements are shown in Table 2.

In most cases, the in-plane CTE of the powder film or laminate is more balanced than the equivalent product formed by feeding extruded film into the press. This CTE balance is demonstrated in Figure 3 for 2 mil films. There is also a significant difference in the Z-direction (thickness direction) CTE between powder and film based products. The Z-direction CTE is consistently lower for the powder based products in film, single sided laminate, or double sided laminate, in all thicknesses. Fig. 4 shows the comparisons for 2 and 4 mil double sided laminate film.

TABLE 1 - PHYSICAL PROPERTIES OF FILM

DESCRIPTION OF SAMPLE	THICKNESS (MILS)	TENSILE STRENGTH (Kpsi)		TENSILE MODULUS (Kpsi)		TENSILE ELONGATION (%)		SHRINKAGE AT 190°C (%)		TEAR STRENGTH (g/MIL)	
		MD	TD	MD	TD	MD	TD	MD	TD	MD	TD
2 X 2 mil film	4	21.2	9.5	636	432	12.3	6.2	-0.45	0.65	64	*
2 mil film	2	18.2	18.6	672	626	14.3	11.1	0.00	0.11	*	7.5
powder	2	7.1	5.3	630	541	1.5	1.2	-0.09	0.48	7.5	*
powder	4	14.2	5.8	535	397	6.9	2.9	0.07	0.72	21	*
powder	5	9.0	14.7	464	580	4.7	6.6	0.49	-0.79	*	40
2 mil extruded film	2	92	7.1	3300	270	3.7	42	-0.17	0.60	7	*

* Test Invalid - Sample Tore Transverse to Test Direction

TABLE 2 - CTE OF FILM AND LAMINATE

Sample Type	LCP CONSTRUCTION	THICKNESS (MILS)	CTE FROM 0 TO 100°C (ppm/°C) MD	TD	Z
Heat Treated Film	2 x 2 Mil Film	4	4	44	103
Heat Treated Film	2 Mil Film	2	61	10	127
Heat Treated Film	Powder	2	46	52	110
Double Sided Laminate	2 x 2 Mil Film	4	31	44	120
Double Sided Laminate	2 Mil Film	2	72	58	92
Double Sided Laminate	Powder	4	70	47	80
Double Sided Laminate	Powder	2	35	64	81
Heat Treated Film	Powder	4	29	80	103
Single Sided Laminate	2 X 2 Mil Film	4	14	45	118
Single Sided Laminate	2 Mil Film	2	14	78	109
Single Sided Laminate	Powder	4	22	41	99
Single Sided Laminate	Powder	2	19	72	91
Heat Treated Film	Powder	5	56	36	107
Extruded Film	2 Mil Control	2	-14	87	119

Another important parameter in the manufacture of laminate for printed circuit boards is dimensional stability. This is the change in dimension as the laminate is etched and subjected to an oven temperature at about 150°C. Table 3 compares the dimensional stability of powder and film based 2 and 4 mil double sided copper foil laminates produced in this test. The powder based laminate is more balanced than the film based product in each case for both 2 mil and 4 mil thicknesses, and for "as etched" and "after bake" measurements.

TABLE 3 - DIMENSIONAL STABILITY OF DOUBLE-SIDED LAMINATE

LAMINATE CONSTRUCTION	DIMENSIONAL STABILITY AS ETCHED (%)		DIMENSIONAL STABILITY AFTER BAKE (%)	
	MD	TD	MD	TD
2 X 2 Mil Film	0.00	-0.22	-0.04	-0.38
2 Mil Film	0.08	-0.46	0.27	-0.72
4 Mil Powder	-0.27	-0.47	-0.40	-0.80
2 Mil Powder	-0.37	-0.40	-0.47	-0.63

Figure 5 demonstrates the improved balance for the 2 mil laminate prepared from powder as measured after bake.

CLAIMS

What is claimed is:

1. A process for producing a continuous liquid crystal polymer film material having a balanced dimensional stability comprising:

(a) uniformly spreading a layer of powder particles of said polymer on a flat surface, said particles having an average particle size in the range of about 0.5 to about 250 microns;

(b) superimposing a second flat surface over said uniformly spread particles to form a sandwich structure;

(c) subjecting said sandwich structure to uniform heat and pressure sufficient to form a nematic melt phase of said polymer, and

(d) cooling said structure to form a liquid crystalline film.

2. The process of claim 1 wherein said particles have an average particle size in the range of about 0.5 to 5 microns.

3. The process of claim 1 wherein said liquid crystal polymer is a polyester or a polyester-amide polymer.

4. The process of claim 3 wherein said polyester or

polyester-amide polymer has a melting point of from about 250° to 375°C.

5. The process of claim 4 wherein said polymer is selected from the group consisting of: a polyester comprising monomer units derived from 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid; a polyester-amide comprising monomer units derived from 6-hydroxy-2-naphthoic acid, terephthalic acid, and acetaminophen; and a polyester comprising monomer units derived from 4-hydroxybenzoic acid, terephthalic acid and 4,4'-biphenyl and mixtures thereof.

6. The process of claim 1 wherein said heating temperature is in the range of from about 25°C below the melting point of said polymer to about 50°C above said melting point.

7. The process of claim 6 wherein said heating temperature is in the range of from about the melting point up to about 15 to 35°C above the melting point of said polymer.

8. The process of claim 1 wherein each of said flat surfaces are release layers adapted to be peeled away from said liquid crystalline film after cooling of said film.

9. The process of claim 1 wherein at least one or both of said flat surfaces is a conductive metal sheet having a thickness of from about 0.25 to 6 mils, which sheet adheres to the surface of said liquid crystalline film after cooling of said liquid crystalline film.

10. The process of claim 9 wherein said metal sheet is a copper film.

11. The process of claim 1 wherein said liquid crystalline film has a thickness of from about 0.25 to 10 mils.

12. The process of claim 11 wherein said liquid crystalline film a thickness of from about 1 to 5 mils.

13. The process of claim 1 wherein said sandwich structure is placed between a pair of moving metal belts and continuously advanced between said belts under heat and pressure.

14. The process of claim 13 wherein the pressure between said moving belts is in the range of about 50 to 600 psi.

15. A liquid crystal film material prepared by the process of claim 1.

16. The film of claim 15 having a sheet of conductive metal adhered to one or both surfaces of said film.

17. The film of claim 16 wherein said conductive metal is copper.

18. A microelectronic circuit board comprising a laminate of one or more dielectric circuit layers comprising the film of claim 15.

FIG. 1

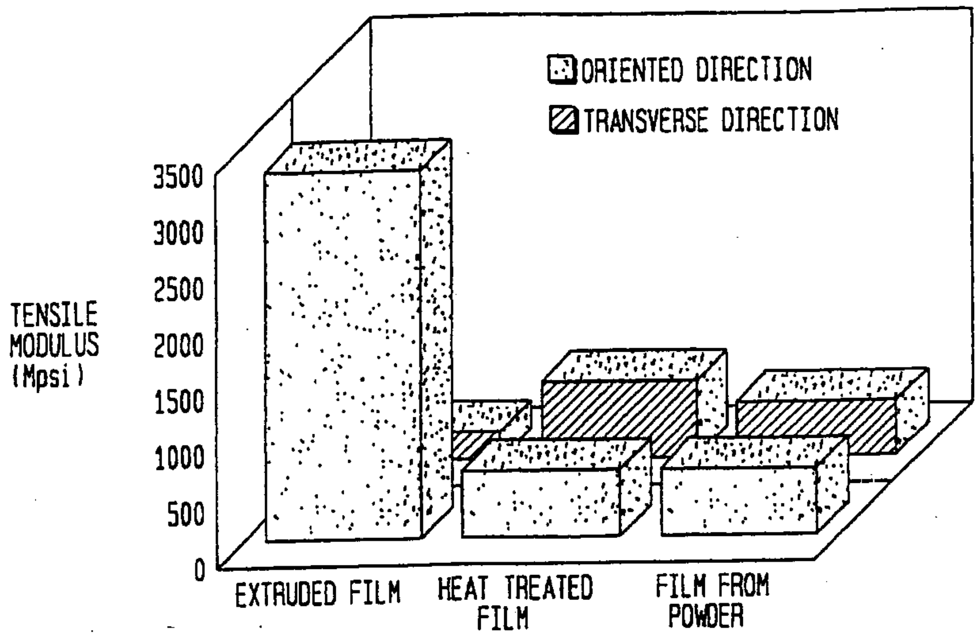

ORIENTED DIRECTION
TRANSVERSE DIRECTION
TENSILE MODULUS (Mpsi)
3500
3000
2500
2000
1500
1000
500
0
EXTRUDED FILM
HEAT TREATED FILM
FILM FROM POWDER

FIG. 2

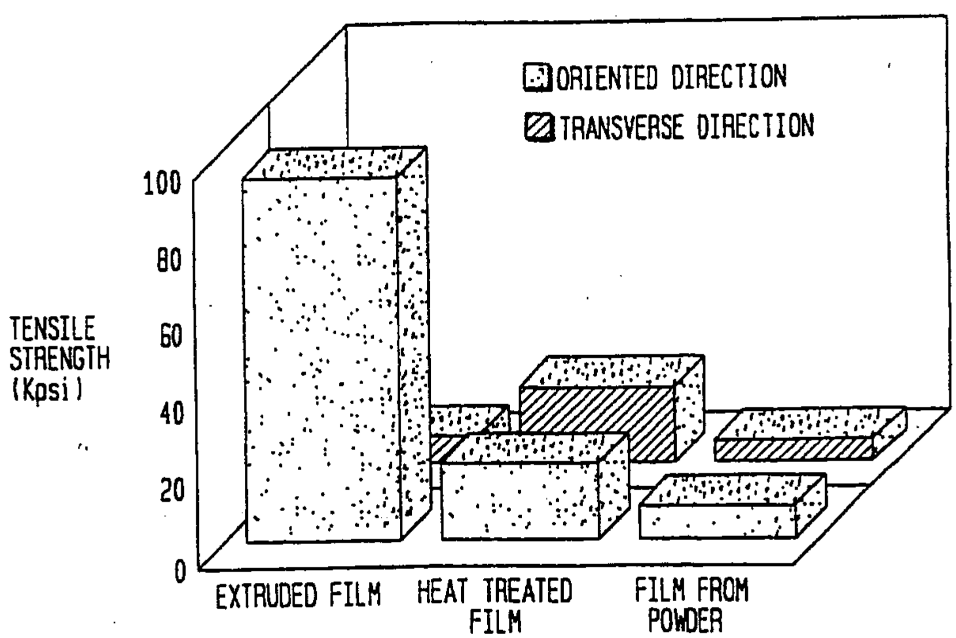

ORIENTED DIRECTION
TRANSVERSE DIRECTION
TENSILE STRENGTH (Kpsi)
100
80
60
40
20
0
EXTRUDED FILM
HEAT TREATED FILM
FILM FROM POWDER

FIG. 3

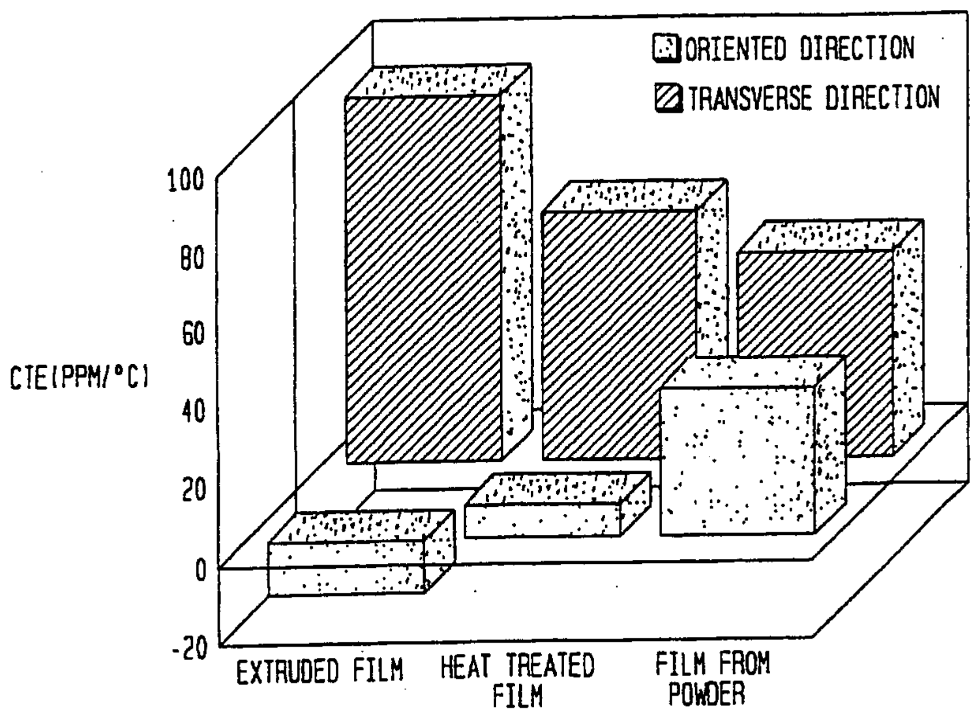

ORIENTED DIRECTION
TRANSVERSE DIRECTION
100
80
60
40
20
0
-20
CTE(PPM/°C)
EXTRUDED FILM
HEAT TREATED FILM
FILM FROM POWDER

FIG. 4

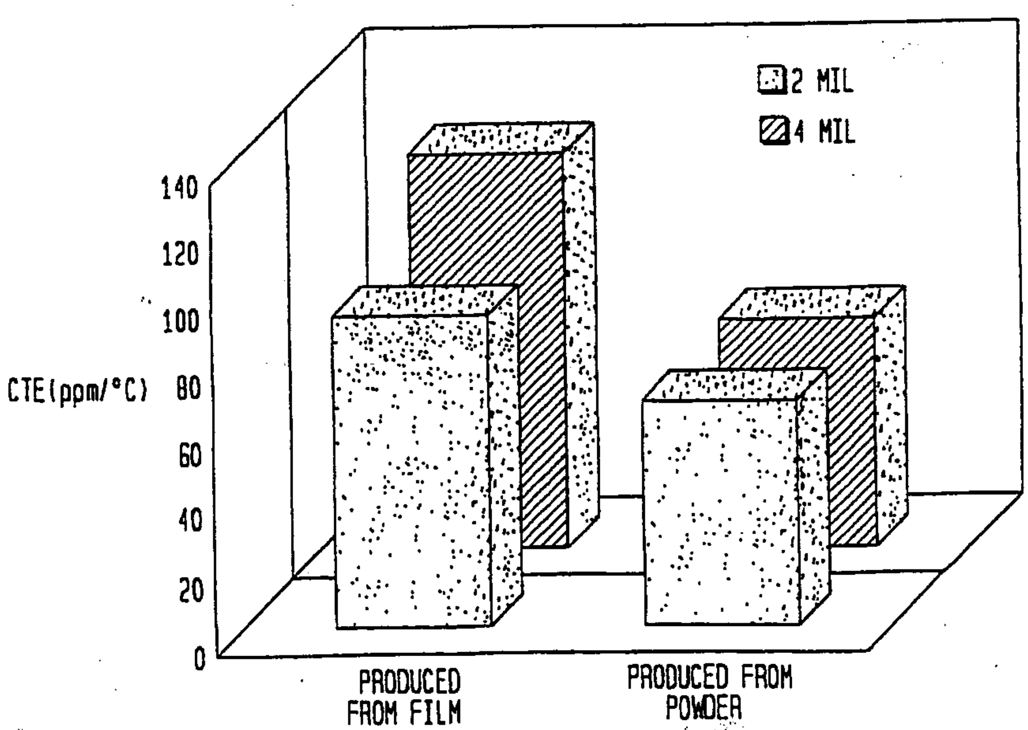
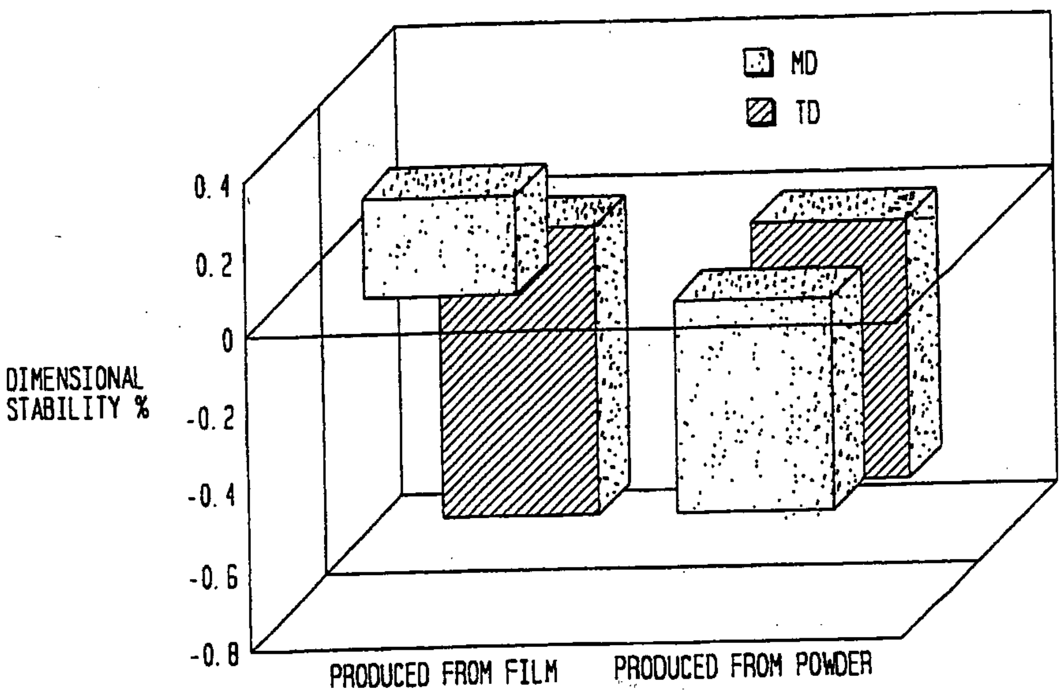

2 MIL
4 MIL
140
120
100
80
60
40
20
0
CTE(ppm/°C)
PRODUCED FROM FILM
PRODUCED FROM POWDER

FIG. 5


MD
TD
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
DIMENSIONAL STABILITY %
PRODUCED FROM FILM
PRODUCED FROM POWDER

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/17059

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J5/18 B32B15/08 B29C43/22 //C08L67:04,C08L77:12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J B32B B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 604 838 (HOECHST CELANESE CORP) 6 July 1994 see the whole document ---	1-18
A	EP,A,0 484 818 (HOECHST CELANESE CORP) 13 May 1992 ---	
A	WO,A,89 12547 (FOSTER MILLER INC) 28 December 1989 ---	
A	EP,A,0 677 368 (JAPAN GORE TEX INC) 18 October 1995 ---	
A	EP,A,0 137 449 (NIPPON PETROCHEMICALS CO LTD) 17 April 1985 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
17 February 1997	28.02.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Tarrida Torrell, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. onal Application No
PCT/US 96/17059

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